METHOD 9056A

DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 This method addresses the sequential determination of chloride (Cl^-), fluoride (F^-), bromide (Br^-), nitrate (NO_3^-), nitrite (NO_2^-), phosphate (PO_4^{3-}), and sulfate (SO_4^{2-}) anions in aqueous samples, such as drinking water, wastewater, aqueous extracts of solids, and the collection solutions from the bomb combustion of solid waste samples.

1.2 The method detection limit (MDL), the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero, varies for anions as a function of sample size. Generally, minimum detectable concentrations are in the range of 0.002-0.02 mg/L for F^-, Br^-, Cl^-, NO_3^--N, NO_2^--N, PO_4^{3-}-P, and SO_4^{2-} with a 50-µL sample loop. Example MDLs for specific anions are given in Table 1 and are provided for illustrative purposes only. The upper limit of the method is dependent on total anion concentration and may be determined experimentally. Maximum column loading (total anions) should not exceed approximately 500 ppm. Dilution of samples may allow higher concentration samples to be analyzed.

1.3 Analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two, Sec. 2.1, for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 method is not mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

2.0 SUMMARY OF THE METHOD

2.1 A small volume of aqueous sample, typically 2 to 3 mL, is injected into an ion chromatograph to flush and fill a constant-volume sample loop. The sample is then injected into a flowing stream of carbonate-bicarbonate eluent.

2.2 The sample is pumped through two different ion exchange columns, then a suppressor device, and into a conductivity detector. The two ion exchange columns, a precolumn or guard column and a separator column, are packed with low-capacity, strongly basic anion exchange resin. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The suppressor is an ion exchange-based device that reduces the background conductivity of the eluent to a low or negligible level and also converts the anions in the sample to their more conductive acid forms. The separated anions in their acid forms are measured using an electrical-conductivity cell. Anions are identified based on their retention times compared to known standards.

Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve generated from known standards.

3.0 DEFINITIONS

Refer to Chapter One and Chapter Three for applicable definitions.

4.0 INTERFERENCES

4.1 Any species with a retention time similar to that of the desired ion will interfere. Large quantities of ions eluting close to the ion of interest will also result in an interference. Separation can be improved by adjusting the eluent concentration and/or flow rate. Sample dilution and/or the use of the method of standard additions can also be used. For example, high levels of organic acids that may interfere with inorganic anion analysis may be present in industrial wastes. Two common species, formate and acetate, elute between fluoride and chloride.

4.2 The water dip or negative peak that elutes near, and can interfere with, the fluoride peak, can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (100 times more concentrated than the solution described in Section 7.3) to 100 mL of each standard and sample.

4.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

4.4 Samples that contain particles larger than 0.45 µm and reagent solutions that contain particles larger than 0.20 µm require filtration to prevent damage to instrument columns and flow systems. The associated method blanks must also be filtered if any samples or reagents have undergone filtration.

4.5 The acetate, formate, and other monovalent organic acids anion elutes early in the chromatographic run and can interfere with fluoride. The retention times of anions may differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples where acetate is used for pH adjustment.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

6.0 EQUIPMENT AND SUPPLIES

6.1 Ion chromatograph - capable of delivering 1 to 5 mL of eluent per minute at a pressure of 1000 to 4000 psi (6.5 to 27.5 MPa). The chromatograph shall be equipped with an injection valve, a 25- to 100-µL sample loop, and set up with the following components, as schematically illustrated in Figure 1.

6.1.1 Precolumn - a guard column placed before the separator column to protect the separator column from being fouled by particulates or certain organic constituents (4 x 50 mm, Dionex IonPac AG4A -SC P/N 43175, or equivalent).

6.1.2 Separator column - see Figure 2. A column packed with low-capacity styrene divinylbenzene-based pellicular anion exchange resin has been found to be suitable for resolving F^-, Br^-, Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^{2-} (4 x 250 mm, Dionex IonPac AS4A-SC P/N 43174, or equivalent).

6.1.3 Suppressor - an ion exchange-based device that is capable of converting the eluent and separated anions to their respective acid forms (Dionex AMMS-II P/N 43074 or ASRS Ultra P/N 53946, or equivalent).

6.1.4 Detector - a low-volume, flow-through, temperature-compensated, electrical conductivity cell (approximately 1.25-µL volume, Dionex CD20, or equivalent) equipped with a meter capable of reading from 0 to 1,000 Siemens/cm on a linear scale.

6.1.5 Pump - capable of delivering a constant flow of approximately 1 to 5 mL/min throughout the test and tolerating a pressure of 1000 to 4000 psi (6.5 to 27.5 MPa).

6.2 Syringe - minimum capacity of 1 mL, equipped with a male pressure fitting.

6.3 Appropriate chromatographic data and control software to acquire data. Dionex PeakNet was used to record and process the chromatogram shown in Figure 2. Alternatively, an integrator or recorder can be used to integrate the area under the chromatographic peaks. If an integrator is used, the maximum area measurement must be within the linear range of the integrator. The recorder should be compatible with the detector output with a full-scale response time of 2 seconds or less. Systems using an integrator or recorder may not necessarily achieve the same MDLs shown in Table 1.

6.4 Analytical balance - capable of weighing to the nearest 0.0001 g.

6.5 Pipets, Class A volumetric flasks, beakers - assorted sizes.

7.0 REAGENTS AND STANDARDS

7.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

7.3 Eluent, 1.7 mM $NaHCO_3$/1.8 mM Na_2CO_3. Dissolve 0.2856 g of sodium bicarbonate (1.7 mM $NaHCO_3$) and 0.3816 g of sodium carbonate (1.8 mM Na_2CO_3) in reagent water and dilute to 2 L with reagent water or follow manufacturer's guidance for the proper eluent for each specific column.

7.4 Suppressor regenerant solution (25 mM H_2SO_4), if required. Add 2.8 mL of concentrated sulfuric acid (H_2SO_4) to 4 L of reagent water.

7.5 Stock solutions (1,000 mg/L). Certified standards may also be purchased and used as stock solutions.

7.5.1 Bromide stock solution (1.00 mL = 1.00 mg Br^-). Dry approximately 2 g of sodium bromide (NaBr) for 6 hours at 150°C, and cool in a desiccator. Dissolve 1.2877 g of the dried salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.5.2 Chloride stock solution (1.00 mL = 1.00 mg Cl^-). Dry sodium chloride (NaCl) for 1 hour at 600°C, and cool in a desiccator. Dissolve 1.6484 g of the dry salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.5.3 Fluoride stock solution (1.00 mL = 1.00 mg F^-). Dissolve 2.2100 g of sodium fluoride (NaF) in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask. Store in a chemical-resistant glass or polyethylene container.

7.5.4 Nitrate stock solution (1.00 mL = 1.00 mg NO_3^-). Dry approximately 2 g of sodium nitrate ($NaNO_3$) at 105°C for 24 hours. Dissolve exactly 1.3707 g of the dried salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.5.5 Nitrite stock solution (1.00 mL = 1.00 mg NO_2^-). Place approximately 2 g of sodium nitrate ($NaNO_2$) in a 125 mL beaker and dry to constant weight (about 24 hours) in a desiccator containing concentrated H_2SO_4. Dissolve 1.4998 g of the dried salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask. Store in a sterilized glass bottle. Refrigerate and prepare monthly.

<u>NOTE</u>: Nitrite is easily oxidized, especially in the presence of moisture, and only fresh reagents are to be used.

<u>NOTE</u>: Prepare sterile bottles for storing nitrite solutions by heating them for 1 hour at 170°C in an air oven.

7.5.6 Phosphate stock solution (1.00 mL = 1.00 mg PO_4^{3-}). Dissolve 1.4330 g of potassium dihydrogen phosphate (KH_2PO_4) in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.5.7 Sulfate stock solution (1.00 mL = 1.00 mg SO_4^{2-}). Dissolve 1.4790 g of the dried salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.6 Anion working solutions

Prepare a blank and at least three different working solutions containing the following combinations of anions. The combination anion solutions must be prepared in Class A volumetric flasks. See Table 2.

7.6.1 Prepare the high-range standard solution by combining the volumes of each anion stock solution specified in Table 2 in a Class A volumetric flask and diluting the mixture to 1 L with reagent water.

7.6.2 Prepare the intermediate-range standard solution by diluting 10.0 mL of the high-range standard solution (see Table 2) to 100 mL with reagent water.

7.6.3 Prepare the low-range standard solution by diluting 20.0 mL of the intermediate-range standard solution (see Table 2) to 100 mL with reagent water.

7.7 Stability of standards

Stock solutions are stable for at least 1 month when stored at 4 ± 2EC. Dilute working standards should be prepared weekly, except those that contain nitrite and phosphate, which should be prepared fresh daily. The validity of standards can be confirmed through the analysis of a freshly prepared ICV (Sec. 9.4).

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

8.2 Samples should be analyzed within 48 hours of collection. Preserve by refrigeration at 4 ± 2EC.

9.0 QUALITY CONTROL

9.1 All quality control data should be maintained and available for easy reference and inspection. Refer to Chapter One for additional quality control guidelines.

9.2 For each batch of samples processed, method blanks must be carried throughout the entire sample preparation and analytical process according to the frequency described in Chapter One. If the samples are filtered, the associated method blanks must also be filtered. These blanks will be useful in determining if samples were contaminated during sample preparation or handling. Refer to Chapter One for the proper protocol when analyzing blanks.

9.3 For each batch of samples processed, at least one laboratory control sample must be carried throughout the entire sample preparation and analytical process as described in Chapter One. The laboratory control samples should be spiked with each analyte of interest at the project-specific action level or when lacking project-specific action levels, between the low and midlevel standards. Acceptance criteria should be set at a laboratory-derived limit developed through the use of historical analyses. In the absence of historical data, this limit should be set at ± 20% of the spiked value. Acceptance limits derived from historical data must be no wider that ± 20%. If the laboratory control sample is not acceptable, then the laboratory control sample must be re-run once. If the results are still unacceptable, then all samples analyzed after the last acceptable laboratory control sample must be reprepared and reanalyzed. Refer to Chapter One for more information.

9.4 After initial calibration, the calibration curve must be verified by use of an initial calibration verification (ICV) standard. The ICV standard must be prepared from an independent (second source) material at or near the mid-range of the calibration curve. The acceptance criteria for the ICV standard must be no greater than ± 10% of its true value. If the calibration curve cannot be verified within the specified limits, the cause must be determined and the instrument recalibrated before samples are analyzed. The analysis data for the ICV must be kept on file with the sample analysis data.

9.5 The calibration curve must be verified at the end of each analysis batch and/or after every 10 samples by use of a calibration blank and a continuing calibration verification (CCV) standard. The CCV should be made from the same material as the initial calibration standards at or near mid-range. The acceptance criteria for the CCV standard must be ± 10% of its true value and the calibration blank must not contain target analytes above 2-3 times the MDL in order for the calibration to be considered valid. If the calibration cannot be verified within the specified limits, sample analysis must be discontinued, the cause determined, and the instrument recalibrated. All samples analyzed after the last acceptable CCV/calibration blank must be reanalyzed. The analysis data for the CCV/calibration blank must be kept on file with the sample analysis data.

9.6 Method detection limit (MDL)

MDLs should be established for all analytes using reagent water (blank) fortified at a concentration of approximately 3 times the estimated instrument detection limit. To determine MDLs, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations described in the method and report concentration values in the appropriate units.

9.7 Matrix spike/matrix spike duplicates (MS/MSDs)

MS/MSDs are intralaboratory split samples spiked with identical concentrations of target analytes. The spiking occurs prior to sample preparation and analysis. An MS/MSD pair is used to document the bias and precision of a method in a given sample matrix. MS/MSDs should be analyzed at the frequency of one per analytical batch, as described in Chapter One. Refer to the definitions of bias and precision in Chapter One for the proper data reduction protocols. Each laboratory should calculate its own acceptance criteria based on its historical data for each matrix type. Refer to Chapter One for guidance.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Establish ion chromatographic operating parameters equivalent to those indicated in Table 1, or as recommended by the manufacturer.

10.2 For each analyte of interest, prepare a blank and calibration standards at a minimum of three concentrations by adding accurately measured volumes of one or more stock standards to a Class A volumetric flask and diluting to volume with reagent water. If the working range exceeds the linear range of the system, a sufficient number of standards must be analyzed to allow an accurate calibration curve to be established. One of the standards should be representative of a concentration near, but above, the method detection limit if the system is operated on an applicable attenuator range. The other standards should correspond to the range of concentrations expected in the sample or should define the working range of the detector. Unless the attenuator range settings are proven to be linear, each setting must be calibrated individually. The calibration curve should be prepared every 12 hours of operation.

10.3 Using a fixed injection volume between 25 and 100 mL (determined by injection loop volume) of each calibration standard, tabulate peak area (preferably) or height responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded.

10.4 The working calibration curve must be verified on each working day, or whenever the anion eluent strength is changed, and for every batch of samples, by injection of a CCV standard (Sec. 9.5). If the response or retention time for any analyte varies from the expected (i.e., previous) values by more than ± 10%, then the test must be repeated, using fresh calibration standards. If the results are still more than ± 10%, then an entirely new calibration curve must be prepared for that analyte.

10.5 Nonlinear response can result when the separator column capacity is exceeded (overloading). Maximum column loading (total anions) should not exceed approximately 500 ppm.

11.0 PROCEDURE

11.1 Sample preparation

When aqueous samples are injected, the water passes rapidly through the columns, and a negative "water dip" is observed that may interfere with the early-eluting fluoride and/or chloride ions. The water dip should not be observed in combustate samples since the collecting solution is a concentrated eluent solution that will be equivalent to the eluent strength when diluted to 100-mL with reagent water according to the bomb combustion procedure. Any dilutions required in analyzing other water samples should be made with the eluent solution. The water dip, if present, may be removed by adding concentrated eluent to all samples and standards to result in a final sample/standard solution that is equivalent to bicarbonate/carbonate concentration of the eluent. When a manual system is used, it is necessary to micropipet concentrated buffer into each sample. The recommended procedures follow:

11.1.1 Prepare a 100-mL stock of eluent 100 times normal concentration by dissolving 1.428 g $NaHCO_3$ and 1.908 g Na_2CO_3 in 100 mL of reagent water or use the manufacturer's specified eluent. Cover or seal the volumetric flask .

11.1.2 Pipet 5 mL of each sample into a clean polystyrene micro-beaker. Micropipet 50 mL of the concentrated buffer into the beaker and stir well.

11.1.3 Dilute the samples with eluent, if necessary, to concentrations within the linear range of the calibration.

11.2 Sample analysis

11.2.1 Start the flow of regenerant through the suppressor device, if required. Alternatively, apply the appropriate current to the suppressor immediately after starting the eluent pump.

11.2.2 Set up the recorder range for maximum sensitivity and any additional ranges needed.

11.2.3 Begin to pump the eluent through the columns. After a stable baseline is obtained (approximately 30 minutes), inject a midrange standard. If the peak area or height deviates by more than ± 10% from that of the previous run, then prepare fresh standards.

11.2.4 Begin to inject standards starting with the lowest concentration standard and increasing in concentration. Calculate the regression parameters for the initial standard curve. Compare these values with those obtained in the past. If they exceed the control limits, then stop the analysis and identify and correct the problem.

11.2.5 Inject an ICV standard. Calculate the concentration from the calibration curve and compare the known value. If the ± 10% control limits are exceeded, then stop the analysis until the problem is found. Recalibration is necessary.

11.2.6 When an acceptable value has been obtained for the ICV standard, begin to inject the samples.

11.2.7 Load and inject a fixed amount of well-mixed sample. Flush the injection loop thoroughly (with at least 5x the loop volume), using each new sample. Use the same size loop for all standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

11.2.8 The width of the retention time window used to make identifications should be based on measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time may be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.2.9 If the response for the peak exceeds the working range of the system, then dilute the sample with an appropriate amount of reagent water or eluent and reanalyze.

11.2.10 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, then spike the sample with an appropriate amount of standard and reanalyze.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Prepare separate calibration curves for each anion of interest by plotting the peak areas or peak heights of the standards against the concentration values. Compute the concentration of each analyte in the sample by comparing the sample peak response with the standard curve. Appropriate chromatography data analysis software may be used to perform the functions described in 12.3 and 12.4.

12.2 Many systems will automatically calculate the sample results, but if your system does not, then the enter the calibration standard concentrations and peak heights from the integrator or recorder into a calculator with linear least squares capabilities.

12.3 Calculate the slope (m) and the intercept (b). The slope and intercept define a relationship between the concentration and instrument response of the form:

$$y_i = mx_i + b$$

where:

y_i = predicted instrument response
m = response slope
x_i = concentration of standard i
b = intercept

Rearrangement of the equation above yields the concentration that corresponds to an instrument response:

$$x_j = \frac{(y_j - b)}{m}$$

where:

x_j = calculated concentration for a sample
y_j = actual instrument response for a sample

and m and b are the calculated slope and intercept from the calibration equation.

12.4 Enter the sample peak area or height into the calculator, and calculate the sample concentration in milligrams per liter.

13.0 METHOD PERFORMANCE

13.1 Examples of single-operator accuracy and precision values for reagent, drinking, and surface water, and mixed domestic and industrial wastewater are listed in Table 3. See EPA Method 300.0 for examples of multiple laboratory determinations of bias for the analytes using an IonPac AS4A column, bicarbonate/carbonate eluent, AMMS suppressor and conductivity detection (see Reference 1).

13.2 Combustate samples

Tables 4 and 5 are based on 41 data points obtained by six laboratories which each analyzed four used crankcase oils and three blends of fuel oil with crankcase oil. Each analysis was performed in duplicate. The oil samples were combusted using Method 5050. Each point represents the duplicate analyses of a sample. One point was judged to be an outlier and was not included in the results.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasiblely reduced at the source, the Agency recommends recycling as the next best option.

14.2 The quantity of the chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society, 1155 16th Street, NW, Washington D.C. 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society.

16.0 REFERENCES

1. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Office of Research and Development, USEPA Method 300.0,"Determination of Inorganic Anions by Ion Chromatography," EPA-600/R-93-100, August 1993.

2. Annual Book of ASTM Standards, Volume 11.01 Water, "Test Method for Anions in Water by Chemically-Suppressed Ion Chromatography," D 4327-97, 1998.

3. Standard Methods for the Examination of Water and Wastewater, Method 4110, "Determination of Anions by Ion Chromatography," 18th Edition of Standard Methods, 1992.

4. Dionex, DX-500 System Operation and Maintenance Manual, Dionex Corp., Sunnyvale, CA 94086, 1996.

5. A. Gaskill, E.D. Estes, D.L. Hardison, and L.E. Myers, "Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels," prepared for U.S. Environmental Protection Agency Office of Solid Waste, EPA Contract No. 68-01-7075, WA 80, July 1988.

17.0 TABLES, DIAGRAMS, FLOW CHARTS AND VALIDATION DATA

The pages to follow contain Tables 1 through 5, Figures 1 and 2, and a flow diagram of the method procedure.

TABLE 1

SUGGESTED CHROMATOGRAPHIC CONDITIONS AND
EXAMPLE METHOD DETECTION LIMITS IN REAGENT WATER

Analyte	Retention Time (min)[a]	Method Detection Limit (mg/L)
Fluoride	1.2	0.005
Chloride	1.7	0.015
Nitrite-N	2.0	0.004
Nitrate-N	3.2	0.002
o-Phosphate-P	5.4	0.003
Sulfate	6.9	0.020

[a]The retention time given for each anion is based on the equipment and analytical conditions described in the method and summarized below. Use of other analytical columns or different eluent concentrations will affect retention times accordingly.

Data are taken from Reference 1 and are provided for illustrative purposes only.

Chromatographic Conditions:	
Columns	See Secs. 4.1.1 through 4.1.3
Detector	See Sec. 4.1.4
Eluent	See Sec. 5.3
Sample loop	50 µL
Pump Flow rate	2.0 mL/min

Concentration of Mixed Standard (mg/L):	
Fluoride	2.0
Chloride	3.0
Nitrite-N	2.0
Nitrate-N	5.0
o-Phosphate-P	2.0
Sulfate	15.0

TABLE 2

SUGGESTED PREPARATION OF STANDARD SOLUTIONS
FOR INSTRUMENT CALIBRATION

		Concentration of Standard in mg/L		
Analyte	Volume of Stock Solution (in mL) used to prepare the High-Range Standard[1]	High-Range Standard	Intermediate-Range Standard	Low-Range Standard
Fluoride (F^-)	10	10	1.0	0.2
Chloride (Cl^-)	10	10	1.0	0.2
Nitrite (NO_2^-)	20	20	2.0	0.4
Phosphate (PO_4^{3-})	50	50	5.0	1.0
Bromide (Br^-)	10	10	1.0	0.2
Nitrate (NO_3^-)	30	30	3.0	0.6
Sulfate (SO_4^{2-})	100	100	10.0	2.0

[1]Volumes of each stock solution (1.00 mL = 1.00 mg) that are combined in a Class A volumetric flask and diluted to 1 L to prepare the high-range calibration standard (refer to Sec. 7.5).

The intermediate-range standard is prepared by diluting a volume of the high-range standard, as described in Sec. 7.6.2.

The low-range standard is prepared by diluting a volume of the intermediate-range standard, as described in Sec. 7.6.3.

TABLE 3

EXAMPLE SINGLE-OPERATOR ACCURACY AND PRECISION

Analyte	Sample Type	Spike (mg/L)	Mean Recovery (%)	Std. Dev. (mg/L)
Chloride	RW	0.050	97.7	0.0047
	DW	10.0	98.2	0.289
	SW	1.0	105.0	0.139
	WW	7.5	82.7	0.445
Fluoride	RW	0.24	103.1	0.0009
	DW	9.3	87.7	0.075
	SW	0.50	74.0	0.0038
	WW	1.0	92.0	0.011
Nitrate-N	RW	0.10	100.9	0.0041
	DW	31.0	100.7	0.356
	SW	0.50	100.0	0.0058
	WW	4.0	94.3	0.058
Nitrite-N	RW	0.10	97.7	0.0014
	DW	19.6	103.3	0.150
	SW	0.51	88.2	0.0053
	WW	0.52	100.0	0.018
o-Phosphate-P	RW	0.50	100.4	0.019
	DE	45.7	102.5	0.386
	SW	0.51	94.1	0.020
	WW	4.0	97.3	0.04
Sulfate	RW	1.02	102.1	0.066
	DW	98.5	104.3	1.475
	SW	10.0	111.6	0.709
	WW	12.5	134.9	0.466

All data are taken from Reference 1 and are based on the analyses of seven replicates.

RW = Reagent water
DW = Drinking water
SW = Surface water
WW = Wastewater

TABLE 4

EXAMPLE REPEATABILITY AND REPRODUCIBILITY DATA FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND ION CHROMATOGRAPHY

Average Value, µg/g	Repeatability, µg/g	Reproducibility, µg/g
500	467	941
1,000	661	1,331
1,500	809	1,631
2,000	935	1,883
2,500	1,045	2,105
3,000	1,145	2,306

All data are taken from Reference 5 and are provided for illustrative purposes only.

TABLE 5

EXAMPLE RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND ION CHROMATOGRAPHY

Amount Expected (µg/g)	Amount Found (µg/g)	Bias (µg/g)	Bias (%)
320	567	247	+77
480	773	293	+61
920	1,050	130	+14
1,498	1,694	196	+13
1,527	1,772	245	+16
3,029	3,026	-3	0
3,045	2,745	-300	-10

All data are taken from Reference 5 and are provided for illustrative purposes only.

FIGURE 1

SCHEMATIC OF ION CHROMATOGRAPH

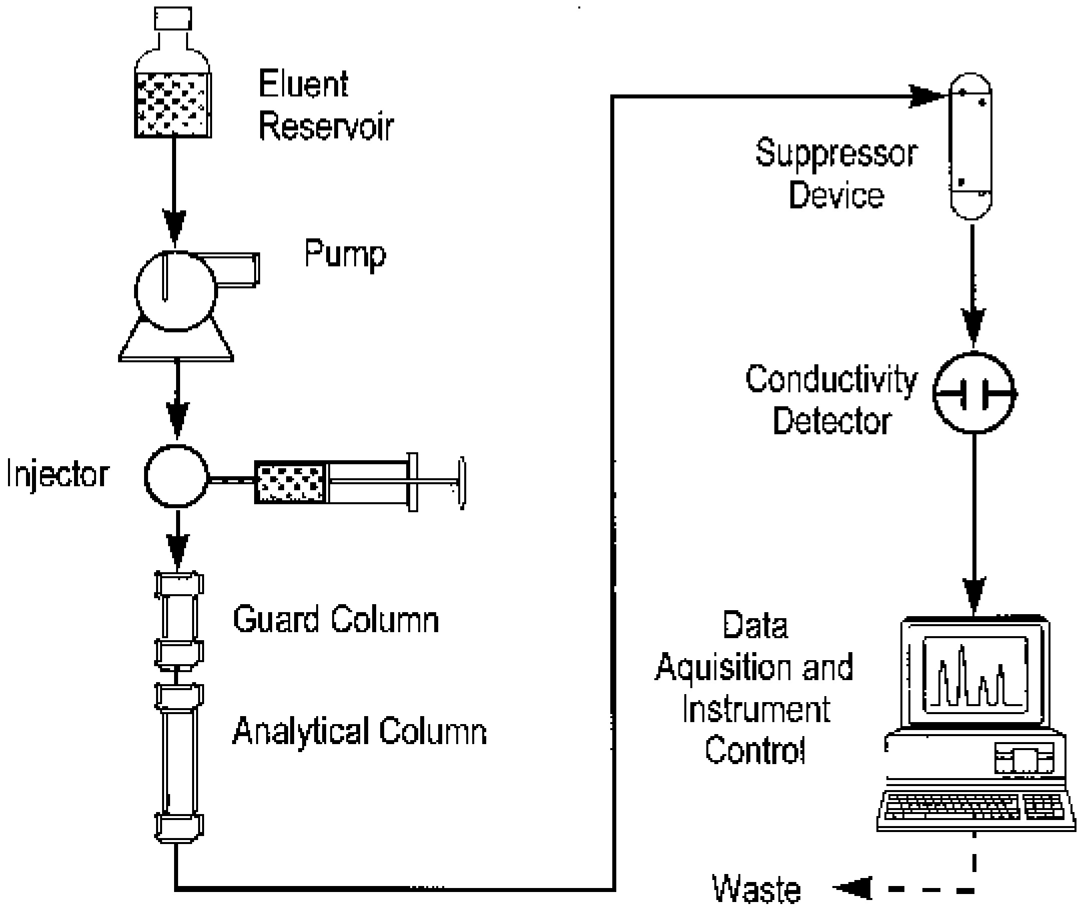
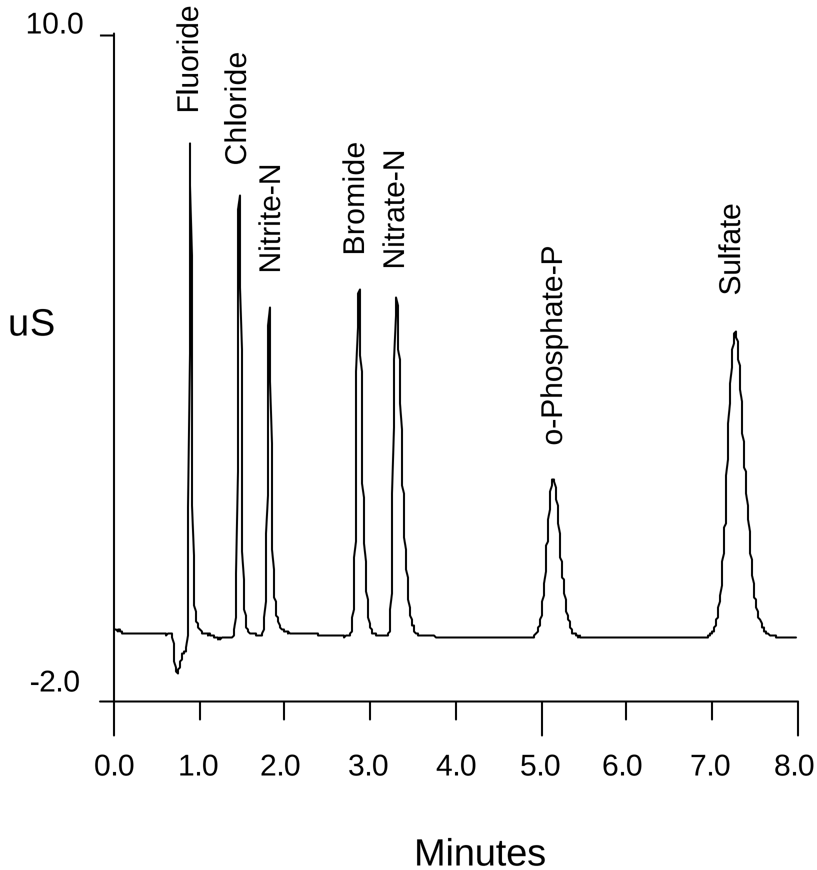
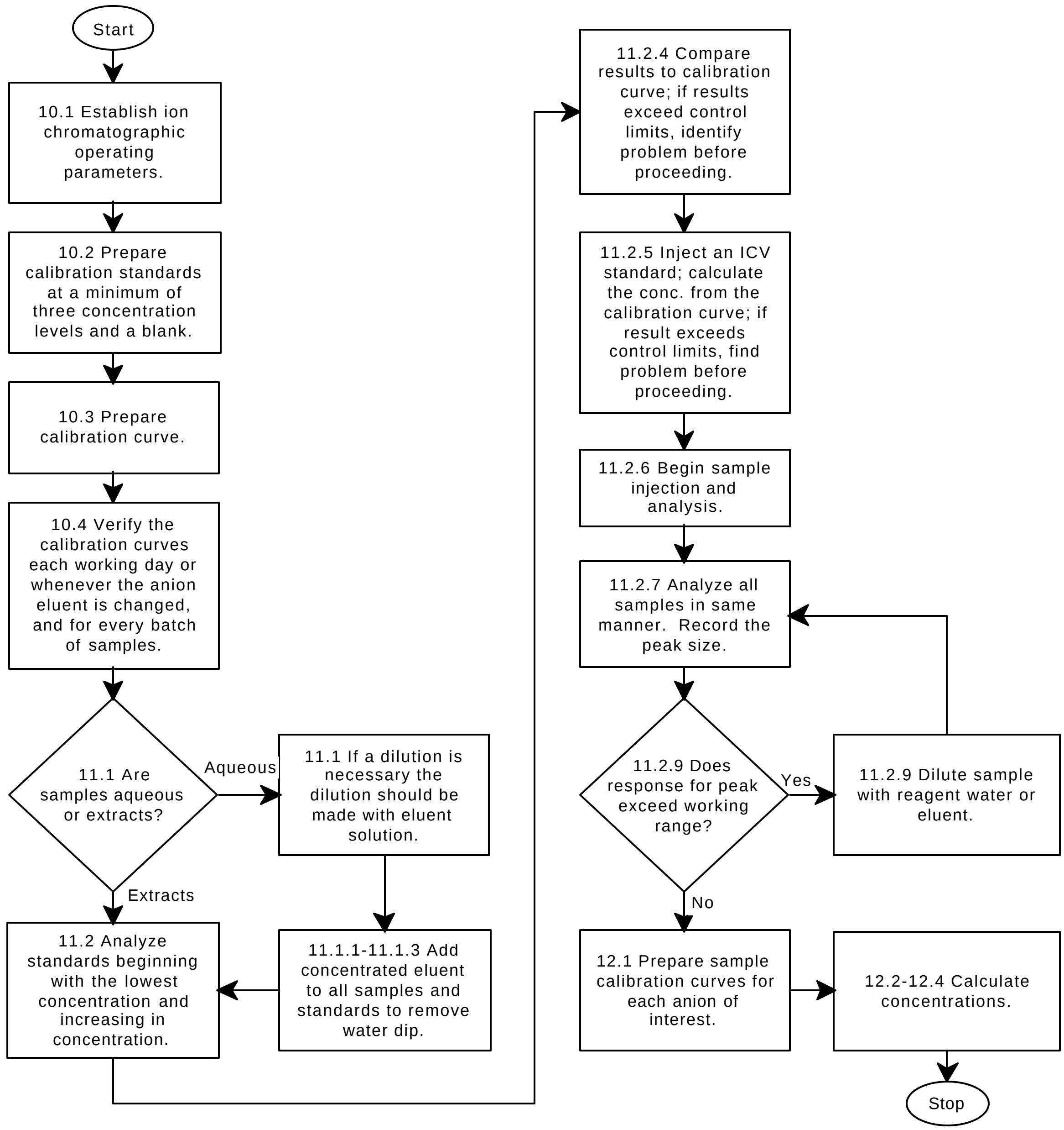


FIGURE 2

EXAMPLE ANION PROFILE



This figure is provided for illustrative purposes only.


Start
10.1 Establish ion chromatographic operating parameters.
10.2 Prepare calibration standards at a minimum of three concentration levels and a blank.
10.3 Prepare calibration curve.
10.4 Verify the calibration curves each working day or whenever the anion eluent is changed, and for every batch of samples.
11.1 Are samples aqueous or extracts?
Aqueous
11.1 If a dilution is necessary the dilution should be made with eluent solution.
11.1.1-11.1.3 Add concentrated eluent to all samples and standards to remove water dip.
Extracts
11.2 Analyze standards beginning with the lowest concentration and increasing in concentration.
11.2.4 Compare results to calibration curve; if results exceed control limits, identify problem before proceeding.
11.2.5 Inject an ICV standard; calculate the conc. from the calibration curve; if result exceeds control limits, find problem before proceeding.
11.2.6 Begin sample injection and analysis.
11.2.7 Analyze all samples in same manner. Record the peak size.
11.2.9 Does response for peak exceed working range?
Yes
11.2.9 Dilute sample with reagent water or eluent.
No
12.1 Prepare sample calibration curves for each anion of interest.
12.2-12.4 Calculate concentrations.
Stop